Freezing-Point Behavior of the Ternary Reciprocal Salt Pair System Involving the Cyclohexylamine and Morpholine Salts of Stearic and Palmitic Acids

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IN THE ISOLATION of pure palmitic acid from cottonseed fatty acids by recrystallization of the cyclohexylamine salts (1, 2) it was found advantageous to perform the first crystallization from a mixture of the cyclohexylamine and morpholine salts. The palmitic acid was thus separated as the cyclohexylamine salt, from which it could be regenerated by acidification. By this mixed-amine method the unsaturated fraction of the cottonseed fatty acids can be recovered in the mother liquor as the morpholine salts. These constitute a valuable by-product since they can readily be converted to morpholide derivatives, which are good primary plasticizers for vinyl resins (3).

In order to obtain fundamental information on the freezing-point behavior of the amine salt mixtures in question, the complete freezing-point diagram has been constructed for the reciprocal salt pair system involving cyclohexylamine stearate (CS), cyclohexylamine palmitate (CP), morpholine stearate (MS), and morpholine palmitate (MP). This diagram can be used for selecting the proportion of the two amines which must be used with a given mixture of stearic and palmitic acids to give the maximum yield of the various salts on crystallization.

Experimental Procedure

The pure salts were prepared by mixing equimolar amounts of the acid and the redistilled amine, all Eastman White Label products,[2] and recrystallizing repeatedly from a solvent until there was no change in the freezing point. All recrystallizations were performed from concentrated solutions in centrifugal tubes (4). The products were dried in a vacuum desiccator over solid potassium hydroxide and had the following freezing points and nitrogen analyses: CS, f.p. 93.03°C.; N, 3.68%, theory 3.65%; CP, f.p., 90.56°C.; N, 3.91%, theory 3.94%; MS, f.p., 72.18° C.; N, 3.85%, theory 3.77%; and MP, f.p., 66.70°C.; N, 4.03%, theory 4.08%.

Mixtures *a*, *b*, and *c*, which were used for making up the quasi-binary mixtures, were prepared by mixing the amine salts in the correct proportions and then melting, solidifying, and grinding twice to ensure homogeneity. The compositions in mole % were as follows: Mixture *a*, 60.0% CS and 40.0% MS; Mixture *b*, 40.0% MP and 60.0% MS; Mixture *c*, 46.0% MP and 54.0% MS.

The freezing-point determinations were made by the thermostatic, sealed tube method (5), which involves finding two temperatures a few tenths of a degree apart, at one of which liquefaction is complete and at the other a few crystals persist after a long period of agitation at constant temperature. Care was taken not to heat the freezing point samples much above the melting point to avoid decomposition of the morpholine salt. That no decomposition took place was shown by the reproducibility of the freezing-point determination on the same sample.

Results and Discussion

Freezing-point data were obtained for the following binary and quasi-binary systems: CS–CP, MS–MP, CS–MS, CP–MP, CS–MP, MS–CP, MP–Mixture *a*, CP–Mixture *b*, and CP–Mixture *c*. The results are given in Table I and shown graphically in Figures 1 and 2. The first four systems (Figure 1) were of the simple eutectic type. The contour of the diagrams for the CS–MP and MS–CP systems would ordinarily be interpreted to indicate the formation of the 1:1 molecular compounds CS:MP and MS:CP, re-

TABLE I

Freezing Point Data for Binary and Quasi-Binary Systems

Mole % of A[a]	Freezing point, °C.	Mole % of A[a]	Freezing point, °C.	Mole % of A[a]	Freezing point, °C.
MP–CS system[b]		MS–CS system[b]		MP–CP system[b]	
0.00	93.0	0.00	93.0	0.00	90.6
11.94	87.2	10.94	89.6	12.56	86.4
20.29	83.0	11.77	90.3	20.54	84.0
29.69	78.3	23.57	86.1	31.08	80.3
39.47	72.8	30.25	84.2	39.21	77.2
49.71	66.8	39.78	81.1	50.17	73.0
55.83	62.5	40.76	80.9	59.89	68.8
58.8[c]	60.4[c]	50.17	77.7	60.22	68.7
59.72	60.2	59.23	74.0	69.42	64.0
62.93	59.2	59.57	74.2	72.0[c]	62.5[c]
64.78	58.9	69.99	69.7	72.22	62.6
67.22	57.5	73.0[c]	68.3[c]	73.73	62.9
68.2[c]	57.1[c]	73.24	68.4	75.28	63.2
70.37	57.8	76.81	68.8	79.78	63.9
71.35	58.0	79.10	69.4	89.58	65.4
78.98	60.8	85.09	70.0	100.00	66.7
89.74	64.0	88.88	70.7		
100.00	66.7	100.00	72.2		
MS–CP system[b]		CP–CS system[b]		MP–MS system[b]	
0.00	90.6	0.00	93.0	0.00	72.2
11.14	83.9	11.01	90.7	11.69	70.4
20.20	78.8	20.40	88.6	19.91	69.4
31.09	72.6	29.79	86.1	30.04	68.1
37.42	68.8	39.90	83.2	39.87	66.1
40.86	66.1	51.28	79.9	50.35	64.0
41.0[c]	66.1[c]	53.1[c]	79.3[c]	60.01	61.7
49.65	66.6	59.58	81.0	63.5[c]	60.7[c]
60.02	65.8	69.79	83.5	69.81	61.9
67.35	64.9	79.74	85.7	79.83	63.5
69.42	64.3	88.48	88.0	89.66	65.2
70.6[c]	64.0[c]	100.00	90.6	100.00	66.7
73.24	64.8				
88.97	69.4				
100.00	72.2				
MP–Mixture *a* system[b]		CP–Mixture *b* system[b]		CP–Mixture *c* system[b]	
0.00	81.1	0.00	66.1	0.00	64.9
29.53	69.7	20.52	60.8	20.27	59.6
43.66	62.8	30.70	57.6	29.94	56.7
47.7[c]	60.4[c]	33.3[c]	56.8[c]	30.8[c]	56.4[c]
47.89	60.3	35.60	58.0	35.73	59.1
53.72	59.7	40.65	61.0	40.25	61.9
59.50	58.6	100.00	90.6	100.00	90.6
64.0[c]	57.5[c]				
70.00	59.2				
78.42	61.6				
100.00	66.7				

[a] A is first-mentioned substance.

[b] CP = cyclohexylamine palmitate; CS = cyclohexylamine stearate; MP = morpholine palmitate; MS = morpholine stearate; Mixture *a* = 60.0% CS–40.0% MS; Mixture *b* = 40.0% MP–60.0% MS; Mixture *c* = 46.0% MP–54.0% MS.

[c] Eutectic or peritectic by graphical interpolation.

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

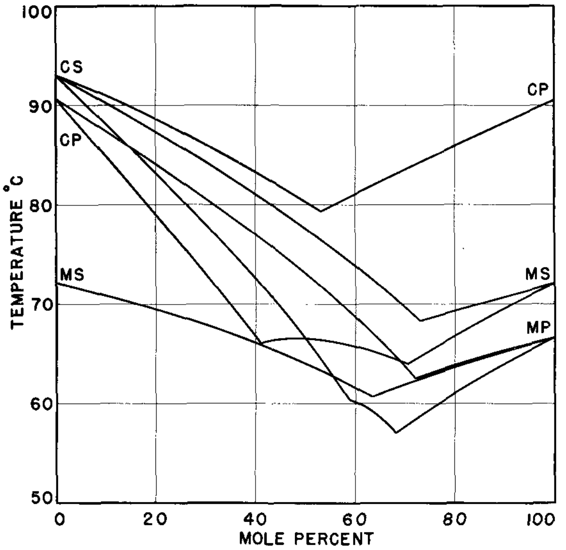

FIG. 1. Binary and quasi-binary freezing-point diagrams in the ternary reciprocal salt pair system involving cyclohexylamine stearate (CS), cyclohexylamine palmitate (CP), morpholine stearate (MS), and morpholine palmitate (MP).

spectively, the former melting incongruently and the latter congruently. However, as shown in a previous publication (6), it must be kept in mind that the individual amine salts, when melted, dissociate into acid and amine molecules, or the corresponding ions. They can therefore undergo double decomposition so that the following equilibrium exists in the liquid state:

$$\mathrm{CS} + \mathrm{MP} \leftrightharpoons \mathrm{MS} + \mathrm{CP}$$

The system involving these four substances is a ternary system of the reciprocal or metathetical type.

The graphical representation of the phase behavior of such systems has been developed by Jänecke (7). Figure 3 is a polythermal projection of the crystallization surfaces of the solid model, formed by plotting primary freezing points vertically above a square base representing the various compositions in mole percentage. Each corner represents a pure substance, the sides represent binary compositions of substances having a common radical, and the interior includes all ternary compositions. Compositions made from a reciprocal pair fall on a diagonal.

The lines E_1P, E_2E, E_3E, E_4P, and EP represent all of the univariant systems, *i.e.*, systems having two solids in equilibrium with the liquid. They correspond to the eutectic grooves formed by the intersections between the four bivariant crystallization surfaces of the solid model. Their positions were defined by finding the temperature and composition of the apparent eutectic or peritectic points in a number of binary and quasi-binary systems (Table I, Figures 1 and 2), projections of which are shown in Figure 3 as broken lines. The position of the eutectic grooves and the compositions and temperatures at the invariant ternary peritectic and eutectic points, P and E, respectively, were further established from isotherms drawn through compositions having identical primary freezing points on each crystallization surface (Figure 4), as determined by interpolation in the various freezing-point diagrams obtained from Table I. (These isotherms were also used to establish the data for the dotted lines in Figure 2). By extrapolation the ternary peritectic composition, P, was thus found to be 34.4 mole % CP, 42.4% MS, and 23.2% MP, and its freezing point was 57.1°C. The corresponding values for the ternary eutectic point, E, are 29.6% CP, 35.2% MS, and 35.2% MP for the composition and 56.2°C. for the temperature.

The various compositions in this diagram are more conveniently expressed in terms of the mole percentage, *c*, of cyclohexylamine in the amine mixture (*i.e.*, the ordinate in Figure 4) and the mole percentage, *p*, of palmitic acid in the acid mixture (*i.e.*, the abscissa). On this basis the composition at the ternary peritectic, *P*, is defined by the values $c = 34.4\%$ and $p = 57.6\%$; and the ternary eutectic, E, by the values $c = 29.6\%$ and $p = 64.8\%$.

The solid model constructed on the basis of Figure 4 is shown in Figure 5. Figure 4 gives a complete picture of the freezing and melting behavior and of the cooling and heating curve behavior of all possible mixtures of cyclohexylamine, morpholine, stearic acid, and palmitic acid in which the total number of moles of acid and amine are equal. Consider, for example, the composition $p = 10\%$, $c = 92\%$, represented by *e* in Figure 6. When a liquid of this composition is cooled to the CS crystallization surface, *i.e.*, the area CS–E_1–P–E_4, crystals of CS will start to separate at 89.0°C. and the composition of the liquid will change along a straight line to e′, where at 64.6°C. both CS and CP will start to crystallize. The liquid composition will then change along E_1P to the peritectic, P, where a new crystalline phase, MS, will appear as the CS crystals redissolve in the liquid according to the following reaction:

$$\text{Liquid} + \mathrm{CS} \leftrightharpoons \mathrm{CP} + \mathrm{MS} + \text{heat.}$$

The temperature will remain constant at 57.1°C. until either the liquid or the crystalline CS is depleted. If, as in the present instance, the original composition is in the area to the left of the MS–CP diagonal, whether in the CS crystallization area or not, the liquid will disappear first and the final solid will consist of crystals of CS, CP, and MS. If, on the other hand, the

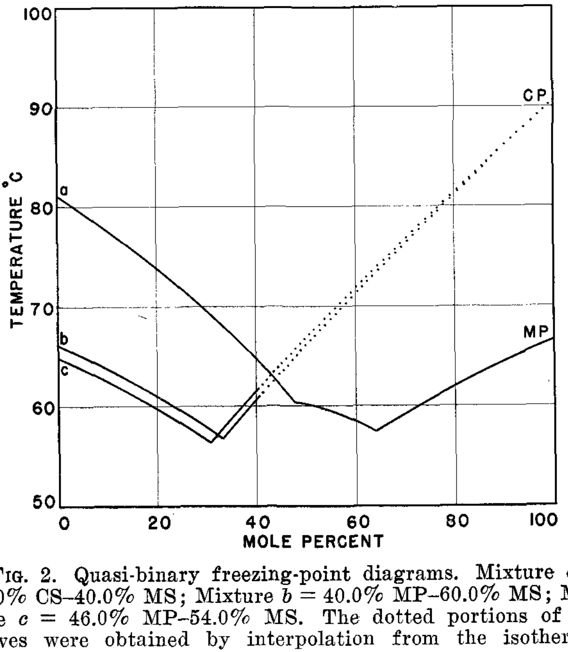

FIG. 2. Quasi-binary freezing-point diagrams. Mixture *a* = 60.0% CS–40.0% MS; Mixture *b* = 40.0% MP–60.0% MS; Mixture *c* = 46.0% MP–54.0% MS. The dotted portions of the curves were obtained by interpolation from the isothermal projection of the solid model for the system.

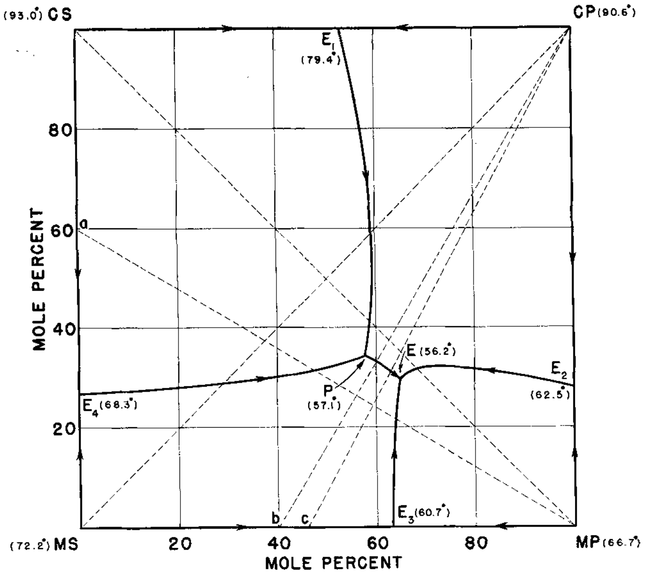

FIG. 3. Polythermal projection of the crystallization surfaces for the ternary reciprocal salt pair system involving CS, CP, MS, and MP. E_1, E_2, E_3, and E_4 are binary eutectics, P is the ternary peritectic, E is the ternary eutectic. The thin broken lines are projections of the quasi-binary systems investigated.

original composition lay to the right of the diagonal and within the triangular area MS–P–CP, the CS crystals would be depleted first. Crystals of MS and CP would then continue to form as the liquid composition changed from P to E, where complete solidification would take place at the constant temperature 56.2°C. In this case the completely solidified sample would consist of crystals of CP, MS, and MP only. No CS crystals would form at any time during the freezing of other compositions to the right of the diagonal. It follows that CP and MS are the "stable salt pair" since they are present in all solidified samples regardless of the original composition.

It is apparent from Figure 3 that the solid phase in equilibrium with the liquid along the middle branch of the CP–MS diagram in Figure 1 is CS and not the 1:1 molecular compound. Contrary to what might be predicted from the contour of the binary freezing-point diagram, an equimolar CP–MS mixture would not freeze at constant temperature. Similarly no molecular compound is formed in the CS–MP and MP–Mixture *a* systems (Figures 1 and 2). The solid phase in equilibrium with the liquid along the middle branch of these diagrams is CP and MS, respectively.

The freezing-point diagram for the reciprocal salt system can be used to calculate the maximum theoretical yield of pure stearic or palmitic acid obtainable from any mixture of the two acids by adding an equivalent amount of cyclohexylamine, morpholine, or any mixture of these two amines, crystallizing, and regenerating the acid from the crystals by acidification. The order in which the various amine salts will crystallize and the change in the composition of the liquid phase with temperature can be deduced from the diagram. It is obvious, for example, that CS will crystallize from composition *e* in Figure 6 and that the maximum yield of CS uncontaminated by palmitic acid salt will be attained when the liquid has reached the composition *e′*. From the values of *p* at *e* and *e′*, 10% and 59.2%, respectively, it can be calculated that 92.3% of the stearic acid present in mixture *e* will crystallize as the amine salt before any palmitic acid salt separates.

When a liquid having the composition *h* is cooled, crystals of MS will form until *h′* is reached and then a mixture of CS and MS will crystallize as the liquid composition changes along h′P to P. CP will then begin to crystallize. The maximum theoretical yield of stearic acid amine salts uncontaminated by palmitic acid salts, as calculated from the values of *p* at *h* and *P*, is 91.8% of the stearic acid present in the original mixture.

TABLE II

Maximum Theoretical Yields of Pure Acids Obtainable by Crystallization of Various Acid and Amine Salt Mixtures

Mixture	Composition of original mixture[a]		Amine-salt recovered	Maximum theoretical yield of acid[c]	
	p	*c*		Stearic	Palmitic
	mole %	*mole %*		%	%
d	10	100.0	CS	90.0	
e	10	92.2	CS	92.3	
f	10	88.6	CS	91.8	
g	10	80.0	CS + MS	91.8	
h	10	6.8	MS + CS	91.8	
i	10	4.6	MS	93.9	
j	10	0.0	MS	93.6	
y[b]	10	....	....	87.8[b]	
k	90	100.0	CP		87.3
l	90	84.6	CP		84.9
m	90	80.0	CP		79.7
n	90	8.4	MP		79.7
o	90	0.0	MP		81.0
z[b]	90	....	....		70.0[b]

[a] *p* = mole % palmitic acid in original palmitic acid–stearic acid mixture; *c* = mole % cyclohexylamine in original cyclohexylamine — morpholine mixture.

[b] Maximum yield obtainable by direct crystallization of the fatty acid mixture.

[c] Percentage of the stearic or palmitic acid in the original mixture recovered.

Table II shows the maximum theoretical yields of pure acid obtainable by the amine salt method from palmitic-stearic acid mixtures containing 90% of stearic or palmitic acid, using the various amine mixtures necessary to give the compositions represented by *d* to *o* in Figure 6. The data for mixtures *y* and *z*

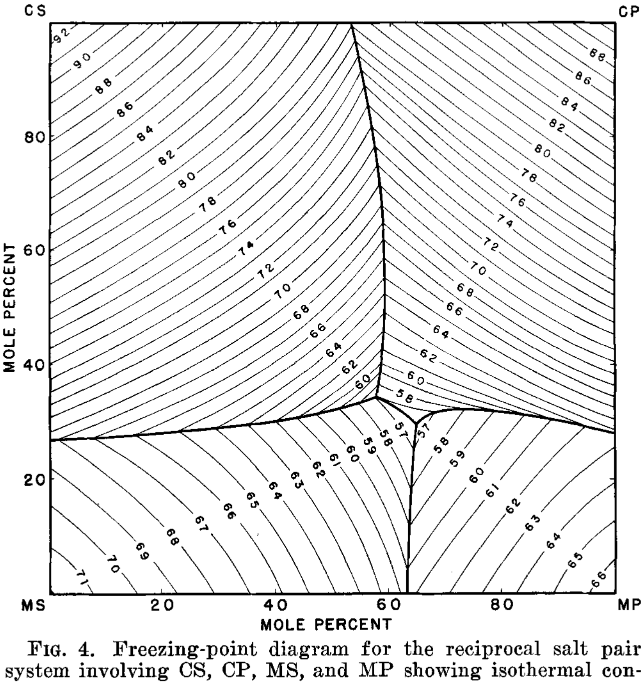

FIG. 4. Freezing-point diagram for the reciprocal salt pair system involving CS, CP, MS, and MP showing isothermal contour projections.

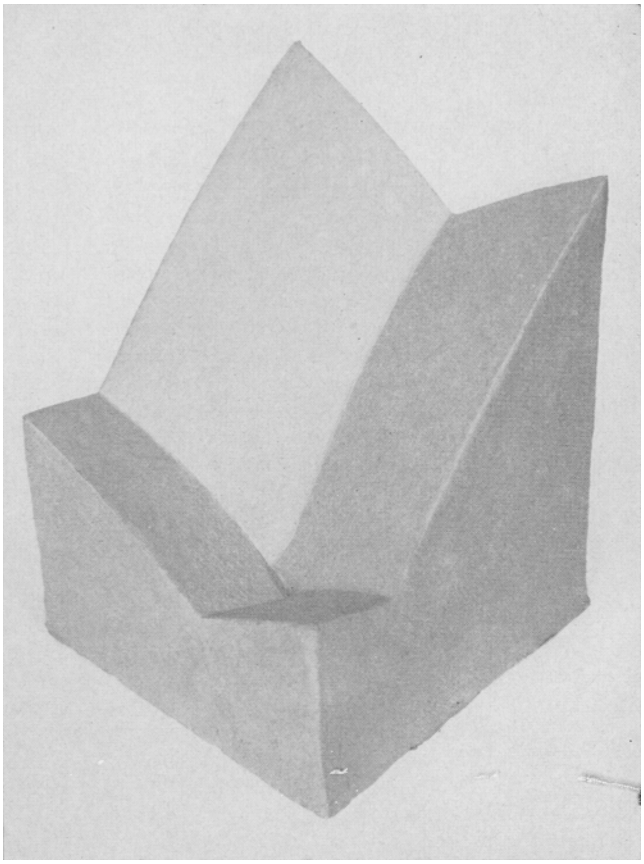

FIG. 5. Three-dimensional model showing the freezing point behavior for the ternary reciprocal salt pair system involving CS, CP, MS, and MP.

in this table show the maximum theoretical yields obtainable by direct crystallization of the fatty acid mixture with no amine added, as calculated from the accepted binary freezing-point data for the two acids (8).

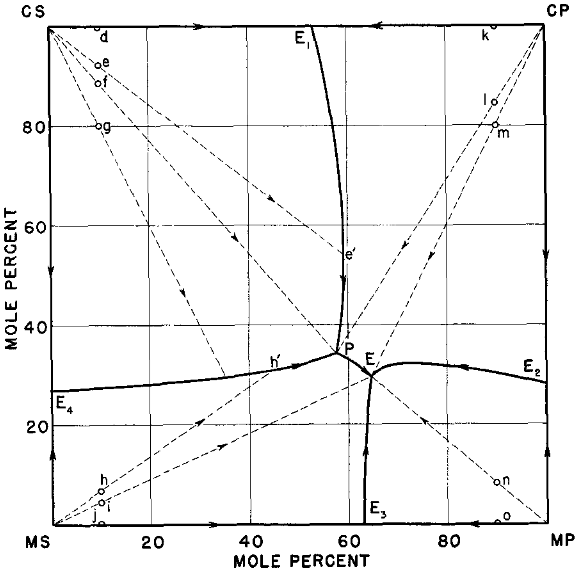

FIG. 6. Polythermal projection of the crystallization surfaces for the ternary reciprocal salt pair system involving CS, CP, MS, and MP showing crystallization paths for various compositions.

Starting with a 90–10% stearic acid–palmitic acid mixture, an 87.8% yield of stearic acid can be obtained by direct crystallization of the acids. This can be increased to 90% by crystallization of the cyclohexylamine salts (composition *d*) and to 93.6% through the morpholine salts (composition *j*). A theoretical yield of 93.9% is attainable by crystallization of the mixed acids with an equivalent amount of a 4.4%–95.6% cyclohexylamine-morpholine mixture (composition *i*). The cyclohexylamine salts have been found to be more effective than the morpholine salts because of more favorable filtration characteristics of the crystals. The maximum yield of the cyclohexylamine salt of stearic acid would be obtained with approximately the proportion of amines used in mixture *e*.

The advantage of amine salt crystallization over direct crystallization of the acids is much more pronounced in the isolation of pure palmitic acid. Thus the theoretical yield obtainable by direct crystallization of a 90%–10% palmitic acid–stearic acid mixture is 70%. The use of morpholine salts alone (composition *o*) results in an 81% yield, and the maximum yield, 87.3%, is attainable by crystallization of the cyclohexylamine salts alone (composition *k*).

Summary

Binary and quasi-binary freezing-point data have been obtained to establish the freezing-point diagram for the ternary reciprocal salt pair system involving cyclohexylamine stearate, cyclohexylamine palmitate, morpholine stearate, and morpholine palmitate. The compositions and freezing points of the ternary peritectic and eutectic mixtures have been determined. Cyclohexylamine palmitate and morpholine stearate are the "stable salt pair." From the diagram it is possible to predict the freezing behavior of any molten mixture of these salts, including the temperature at which crystals of each component will appear on cooling, the yields of these crystals and the composition of the liquid phase at various temperatures, and the temperature at which maximum yields of crystals of the specific salts can be obtained. The data supply fundamental information in connection with the crystallization of mixed amine salts in the purification of palmitic and stearic acids.

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